SCIENCE FOR CERAMIC PRODUCTION

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POSSIBILITIES OF CONCENTRATING KAOLIN FROM THE ZHURAVLINYI LOG DEPOSIT

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The possibility of using kaolin from the Zhuravlinyi Log deposit, which has a great potential with respect to material quality and amount of resources, as a source of non-traditional material is considered. Compositions of obtained ceramic mixtures are indicated.

An important target in stable functioning of enterprises producing aluminosilicate ceramics is securing high-quality kaolin material. It is a historical fact that the Russian Federation has been left without sufficient resources of raw kaolin. The existing concentration factories (based on the Kyshtymskoe, Eleninskoe, and Chalganskoe deposits) satisfy only up to 10% of the Russian need for kaolin, and, moreover, the available kaolin concentrate does not meet the high-grade requirements imposed on its content of pigment oxides, residual content of technological electrolytes (Kyshtymskoe and Chalganskoe kaolin), and mechanical strength and dispersion (Eleninskoe kaolin).

To solve the above problem, it is necessary to involve the Zhuravlinyi Log eluvial deposit of eluvial kaolin, which is a source of non-traditional raw material with great possibilities regarding its quality and quantity [1]. The geological survey of the deposit revealed its veneer bedding of kaolin, the size of which is 500 × 500 m, and the resources of material suitable for industry constitute 7.2 mln tons. A survey carried out at the flanks of the deposit confirmed the existence of an additional 61 mln tons.

The deposit is represented by kaolin of different colors: white, gray, cream, pink, and ochre. The most abundant are the light-colored varieties: white, gray, and cream-colored. The macroscopic kaolin is a non-plastic argillaceous rock of the psammite-pellite composition with quartz grains and mica scales of different sizes. The lithologic varieties of kaolin with different colors have virtually identical granulometric compositions (Fig. 1).

It appears impossible to identify the form of the bedding for each specific variety of kaolin, since the change of the layer coloring from one lithologic variety to another occurs without a visible regularity. At the same time, the boundaries between the light-colored and the tinted varieties can be visually identified, which makes it possible to selectively extract a desired variety.

The studies of the material composition of Zhuravlinyi Log kaolin carried out at the Uralmekhanobr Institute demonstrate that the considered sample is represented by almost totally disintegrated, rather homogeneous rock of sand-clay composition and of grayish-white and yellowish-white color with rare ferruginous sites (lens, spots). The sample texture is earth-like, loosely cemented, and laminar in some sites. The laminar structure is accentuated by heterogeneous impregnation with iron hydroxides. Porosity is occasionally observed. Fragments of quartz and feldspar are cemented by the

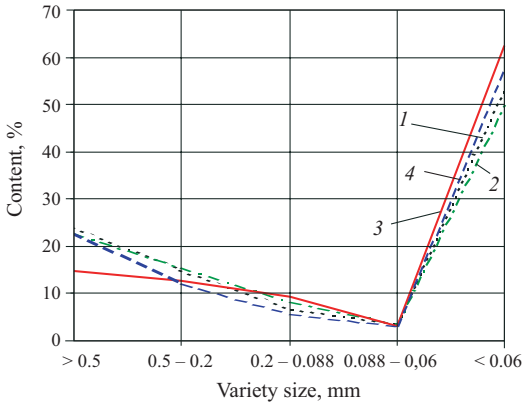

Fig. 1. Granulometric composition of lithologic varieties of the Zhuravlinyi Log kaolin: *1*) white, gray; *2*) cream-colored; *3*) ochre; *4*) pink.

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hydromica-kaolinite mixture with carbonate and mica scales as impurities. The detritus material is mainly represented by different-grained quartz, a small quantity of potash feldspar, which is homogeneous in size, and rare inclusions of carbonate, which are cemented by kaolinite with mica and hydromica and often have laminar orientation.

The kaolinite, which is the main material of the cementing mixture, is compiled by scaly aggregates of different sizes. Worm-shaped aggregates of size 0.05×0.15 and 0.03×0.04 mm are occasionally observed. The kaolinite in polished sections is transparent, clear or yellow. Iron hydroxides non-uniformly impregnate the cementing mixture, in the form of spots, stripes, and lenses, tinting the kaolinite gray-brown. Isolated iron hydroxide inclusions of size less than 0.05×0.05 mm are scattered rather uniformly in the cementing mixture. Rare grains of iron hydroxide have larger sizes up to 0.10×0.10 mm. The sites of purely kaolinite cementing mixture are not big and not too extended; the major part of the rock is represented by kaolinite associated with mica and hydromica with rare inclusions of accessories: monacite, zircon, amphibole, and tourmaline. The size of accessory grains is below 0.05×0.06 mm. The main titanium-containing mineral (leucoxene) is scattered in the cementing material in the form of dots and grains of size below 0.06×0.06 mm.

The quartz prevailing in detritus is uniformly distributed over the cementing mixture. It is represented by different-grained, non-rounded, angular, less often semi-angular fragments of size ranging from 0.15×0.15 to 0.80×0.80 mm. Larger grains of size up to 2 – 5 mm are found. The contacts of the quartz detritus with the cementing mixtures are clearly defined and the grain contours are tortuous and cove-shaped. Quartz in grains is pure, clear, but to a certain degree cracked. Occasional quartz grains in cracks contain dispersed iron hydroxide impurities of size below 0.06×0.06 mm, leucoxene grains, and tourmaline crystals of the same size. The quartz fragments, as a rule, contain inclusions of single long prismatic zircon crystals of size below 0.005×0.050 mm.

The feldspar found in the material is potash feldspar, sometime with a clear microcline lattice, and is nonuniformly distributed. The size of the feldspar grains is significantly smaller than the size of the quartz grains, usually up to 0.12×0.25 mm. The shape of the detritus is angular and irregular, and the contacts with the cementing mixture can be either clearly defined or blurred. The scales and flakes of mica (muscovite) are nonuniformly distributed but usually oriented, which accentuates the microlaminar structure of the rock. The prevailing flake size is below 0.005×0.050 mm; infrequently the size is 0.15×0.15 mm. The mica is partially hydrated and modified to hydromica and kaolinite, and the scale edges are split. Occasional needle-shaped rutile inclusions of size below 0.005×0.050 mm are identified.

Fine carbonate impurities also are nonuniformly distributed in the cementing mixture. Certain sites rich in carbonate detritus are observed. Organic inclusions are insignificant and mostly scattered in the form of black dots [2].

The following conclusions can be drawn on the basis of studying the material composition.

The investigated sample consists of kaolinite (45%), mica or hydromica (6%), and potash feldspar (5%). Iron- and titanium-bearing minerals (about 1%) and carbonates (about 1%) are mainly represented by fine grains and clusters, as well as a small amount of coarse-grained carbonate. They impregnate the cementing kaolinite mixture. Iron hydroxides, hydromica, mica, leucoxene, and other minerals that would contaminate the kaolin concentrate pass to the class below 0.063 mm.

The size and type of contacts of quartz grains in the material make it possible to separate quartz as an individual concentrate using the size classification method.

A significant difference is observed in the size of quartz and feldspar grains. However, the feldspar yield does not exceed 5%, and part of it will pass over to the kaolin concentrate with the argillaceous component.

To obtain kaolin concentrate containing not less than 36% Al_2O_3 (here and elsewhere weight content is indicated), the boundary separation grain should be 20 – 30 μm. At the same time, the finer the kaolin, the larger the iron oxide content, and approximately half of the iron contained in the material is bonded with hydroxides.

Due to the above specifics of the material composition, it appears advisable to test all existent methods for industrial concentration in order to assess the quality of the concentrated product and select the optimal concentration method.

The wet concentration methods ensuring high extraction of the argillaceous component seem to be the most promising. There are electrolyte-free and mono-electrolyte schemes of wet concentration used in the industry. In order to compare the quality of the kaolin concentrate, the Uralmekhanobr Institute investigated the concentration of kaolin using both schemes.

The electrolyte-free scheme involves disintegration in a ball mill of raw kaolin crushed to the size of 25 mm with 40% solid content in the pulp and screening of the mill discharge according to the class 3 mm. Next, the kaolin suspension was screened by size in 3 consecutive stages in a spiral classifier with spiral diameter 150 mm (the main classification) and in hydrocyclones of diameter 75 mm (the first and the second repurifying classification), the discharge of the second repurifying classification yielding concentrated kaolin with a solid content of 15 – 25%. The sand from the main classification operations was then put together, diluted in water, and washed in a spiral classifier producing washed sand, and the classifier overflow was subjected to repurifying classification in a hydrocyclone of diameter 75 mm with the aim of separating kaolin-containing recycling water containing 5 – 15% solid and fine-sands. The qualitative and quantitative parameters resulting from the electrolyte-free concentration are shown in Table 1.

TABLE 1

Concentration product	Yield, %	Mass content, %										Extraction, %			
		Fe_2O_3	TiO_2	Al_2O_3	SiO_2	CaO	MgO	K_2O	Na_2O	SO_3	calcination loss	Fe_2O_3	TiO_2	Al_2O_3	$K_2O + Na_2O$
Class + 3 mm	2.56	0.46	0.07	4.66	90.30	1.24	< 0.10	0.31	0.07	–	2.72	1.9	0.8	0.6	0.8
Concentrated kaolin (discharge of second repurifying classification)	37.55	1.04	0.35	36.20	47.60	0.44	0.28	0.92	0.08	0.01	13.20	4.5	52.0	67.0	31.3
Sand of reference classification	37.74	0.10	0.12	3.03	95.60	0.24	< 0.10	0.50	0.12	–	0.84	6.0	17.9	5.6	19.6
Discharge of repurifying classification	10.29	1.08	0.35	35.40	48.00	–	–	0.88	0.08	–	12.80	18.4	14.3	17.9	8.2
Sand of repurifying classification	11.86	0.47	0.32	15.20	74.30	–	–	3.80	0.24	–	4.28	9.2	15.0	8.9	40.1
Raw kaolin	100	0.61	0.25	20.30	70.00	–	–	1.08	0.11	–	7.17	100	100	100	100

Thus, a sufficiently high yield of kaolin concentrate (37.55%) has been obtained: the concentrate meets the requirements of GOST 21286–82 standard for ceramics and GOST 19285–73 for the paper and cardboard industry with respect to its content of aluminum and iron oxide and dispersion.

In the industrial application of the above scheme, due to the introduction of coagulants before the filter pressing process (for instance, pure milk of lime or milk of lime mixed with polyacrylamide), part of these electrolytes will pass over to the kaolin concentrate. They have a negative effect on the process of liquefying of kaolin before slip casting used in ceramic production.

If kaolin concentrate produced by the above scheme is used as a filler, it has to be additionally dried to 1% moisture, milled, and screened.

The mono-electrolyte scheme consists of concentrating kaolin in concentrated suspensions, when the solid matter content in the initial pulp is 40 – 70%. To increase the fluidity in dense kaolin suspensions, different viscosity-lowering agents are used: liquid glass, sodium polyphosphate, sodium humate, etc. The main concentration scheme is similar to the electrolyte-free scheme, except for the fact that the enriched kaolin after concentration has the form of a dense suspension with a solid content of 35 – 50%. Such a concentrate can be subjected to direct spray drying, eliminating the stages of dehydration through condensation and filtration. The quantitative and qualitative results of the concentration according to the mono-electrolyte scheme are shown in Table 2.

It can be seen that the finished product yield is 36.14%, which is slightly less than in the electrolyte-free scheme. The Fe_2O_3 content in kaolin is the same as in using the electrolyte-free method, but its quality with respect to the Al_2O_3 content is somewhat lower. Therefore, the obtained kaolin does not satisfy all the requirements of the state standard for ceramic articles, but is acceptable for paper and cardboard production.

The advantage of this scheme over the electrolyte-free scheme is obtaining the final product by dehydration in a spray drier, making unnecessary filter pressing, which is obligatory for the electrolyte-free method.

The kaolin concentrate contains residual electrolyte that complicates its use in ceramic slip casting and in other types of production.

In using kaolin as a filling agent, it has to be additionally milled and screened.

TABLE 2

Concentration product	Yield, %	Mass content, %							Extraction, %			
		Fe_2O_3	TiO_2	Al_2O_3	SiO_2	K_2O	Na_2O	calcination loss	Fe_2O_3	TiO_2	Al_2O_3	$K_2O + Na_2O$
Class + 3 mm	2.46	0.22	0.07	5.41	87.90	1.11	0.19	3.56	0.8	0.3	0.6	2.5
Concentrated kaolin (discharge of second repurifying classification)	36.14	1.06	0.32	35.20	48.20	0.95	0.27	12.80	58.8	22.1	62.0	35.2
Sand of reference classification	44.36	0.18	0.53	4.60	93.40	0.98	0.11	1.25	12.3	67.9	9.9	39.1
Discharge of repurifying classification	12.64	1.22	0.28	36.50	46.30	0.46	0.24	13.30	23.7	6.8	22.5	7.1
Sand of repurifying classification	4.40	0.65	0.35	23.10	63.30	4.45	0.27	6.48	4.4	2.9	5.0	16.6
Raw kaolin	100	0.65	0.52	20.52	69.70	1.06	0.19	7.23	100	100	100	100

TABLE 3

Fraction of product, μm	Yield, %	Kaolinite		Mineral composition of non-argillaceous impurities	Whiteness, %
		content, %	extraction, %		
				Intense method	
+ 75	9.6	2	0.40	Mainly quartz (99%) with traces of opaque impurities (ferric oxide)	70
– 75 + 50	11.9	2	0.50	Mainly quartz (90%) with a small quantity of mica (muscovite) flakes	64
– 50 + 25	8.2	6	1.03	Mainly quartz with an insignificant amount of mica	66
– 25 + 10	23.8	40	19.98	Mainly quartz, mica, and kaolinite	65
– 10 + 2.5	29.1	75	45.68	Not determined	68
– 2.5	17.4	89	32.41	The same	69
				Standard method	
+ 500	0.9	1	0.02	Mainly quartz with a small quantity of mica (muscovite) + opaque impurities (ferric oxide) and other rock particles	Not determined
– 500 + 75	17.0	1	0.31	Mainly quartz (95%) with a certain quantity of mica + opaque impurities and rock particles	56
– 75 + 50	6.8	6	0.75	Mainly quartz with an insignificant amount of mica	54
– 50 + 25	11.0	24	4.84	Mainly quartz and mica + kaolinite fillers	54
– 25 + 10	26.6	68	33.25	The same	68
– 10 + 2.5	31.2	86	49.46	Not determined	73
– 2.5	6.5	95	11.37	The same	75

TABLE 4

Method	Mass content, %		
	kaolinite	quartz	mica
Intense, fraction extraction, μm:			
– 2.5	89	7 – 20	< 7
– 10 + 2.5	75	Not determined	
Standard, fraction extraction, μm:			
– 2.5	95	7 – 20	< 7
– 10 + 2.5	86	Not determined	

The dry concentration (air separation) methods, i.e., the intense and the standard one, are no less efficient. The essence of the considered dry concentration scheme consists of preliminary crushing of large lumps, drying of initial material to 1% moisture, milling in a roll mill (for the standard method) or in a hammer mill (for the intense method), classification in a centrifugal air separator, deposition in cyclones, and dust trapping in sleeve tissue filters. The intense concentration method differs from the standard one in finer milling of the initial raw kaolin after drying. The quantitative characteristics of the products obtained by air separation are given in Table 3, and their quantitative characteristics in Tables 4 and 5.

Thus, both methods of dry concentration are sufficiently efficient for producing kaolin concentrate. The yield of the finished product in using the intense method was 37.3%, and that in using the standard method was 39.9%. The concentrated kaolin it its content of Al_2O_3 and Fe_2O_3 satisfies the state standard requirement for ceramics and for paper production.

TABLE 5

Method	Mass content, %															Kaolinite concentrate whiteness, %	
	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	Mn_3O_4	MgO	CaO	Na_2O	K_2O	P_2O_5	Cr_2O_3	SrO	ZrO_2	BaO	calcination loss	non-fired	fired
Intense, fraction extraction, μm:																	
– 2.5	47.14	0.50	36.39	1.82	0.01	0.17	0.22	0.04	0.50	0.04	Not determined				13.04	69	74
– 10 + 2.5	52.70	0.27	32.20	2.31	0.02	0.13	0.21	0.05	0.74	0.02	0.15	0.00	0.04	0.01	10.72	68	Not determined
Standard, fraction extraction, μm:																	
– 2.5	46.27	0.58	37.43	1.04	0.01	0.16	0.22	0.04	0.31	0.04	Not determined				14.04	75	90
– 10 + 2.5	48.87	0.36	35.30	1.66	0.01	0.15	0.24	0.04	0.71	0.03	0.08	0.00	0.03	0.01	12.22	73	Not determined

The extraction of the fraction – 2.5 μm is nearly 3 times higher in using the intense method, due to extra milling of the initial material; however, the iron oxide content in this case becomes higher, and the aluminum oxide content becomes lower. The whiteness index is 69% in non-fired concentrate and 74% in the kaolin concentrate fired at a temperature of 1180°C, against 75 and 90% in the concentrate produced by the standard method.

Such a concentrate can be used without restrictions in other sectors of industry and does not require additional drying, milling, and separation.

In using these methods on an industrial concentration line, in principle it is possible to extract kaolin concentrate of different degrees of dispersion at different points of the line, which will make it possible to form a finished product with prescribed dispersion parameters.

In comparing the intense and the standard methods of dry concentration of kaolin, as well as electrolyte-free and mono-electrolyte wet concentration schemes, the most promising is the standard dry concentration method. This method, taking into account its technological, economic, and environmental aspects, was preferred in designing a concentration production facility at the Zhuravlinyi Log kaolin deposit.

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